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COMPLETE SPECIFICATION.

Non-Shrinking Filling, Casting and Moulding Compositions.

We, DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT VORMALS ROESSLER, of 9 Weissfrauenstrasse, Frankfurt (Main) 1, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :

This invention relates to filling, casting and moulding compositions with a polyester base, which can be cured without shrinkage.

Filling, casting and moulding compositions with a base of unsaturated polyester resins are simple to use, cure rapidly and have good strength values but show relatively large shrinkage during curing, so that hitherto it was not possible for such compositions to be used for technical purposes. The moulded elements which are produced from unsaturated polyester resins, together with other monomeric polymerisable compounds, generally show a shrinkage of up to 10% and more. Apart from the fact that such a shrinkage is untenable for many manufacturing purposes, the mouldings show relatively large internal strains, which can easily lead to cracks. It has already been attempted to reduce this shrinkage by adding relatively large quantities of fillers. It is generally only possible for the shrinkage to be reduced to about 3% by such means.

It is also known, for the manufacture of dimensionally accurate moulded elements from unsaturated polyesters and polymerisable compounds, for a portion of the materials first of all to be completely polymerised outside the mould, for the resulting polymers to be comminuted and for the small particles thus obtained to be introduced into

the mould. The cavities between the particles are then filled by a liquid mixture of the same components and this mixture is thereafter polymerised.

For the same purpose, it is also known to employ as casting resin a mixture of unsaturated polyesters with a high percentage solution of one or more thermoplastic polymers, such as polystyrene, polyvinyl ether and polyisobutylene in styrene.

Furthermore, it is known to use an unsaturated dicarboxylic acid and 2-methylene-1, 3-propane diol in addition to a monomeric polymerisable compound when producing moulded elements.

Finally, it is also known to manufacture colourless crystal-clear casting from mixtures which consist of saturated polyesters, preferably those with terminal hydroxyl groups, and unsaturated polyesters in the ratio of 1.5 : 2 or 1 : 1.

It has now been found that filling, casting and moulding compositions which essentially contain at least one unsaturated hardenable polyester resin, at least one monomeric polymerisable compound containing a vinyl group, at least one saturated polyester plasticiser a redox polymerisation catalyst and, if desired also contain fillers, can be hardened or cured without shrinkage in practice if the constituents of these compositions are chosen as follows : the unsaturated polyester resin must be capable of strong cross-linking ; the plasticiser must be miscible with the uncured components, but be incompletely miscible with the cured mixture, thus causing a certain limited lack of homogeneity which is usually expressed in the form of a clouding. This clouding does not of course occur when the plasticiser and

cured material have the same refractive indices. The plasticiser should be present in quantities from 3 to 30% by weight, advantageously 7 to 25% by weight, calculated on the organic components. Furthermore, it is necessary for the content of monomeric polymerisable compound containing a vinyl group to amount to 10 to 70% by weight, likewise based on the organic components. It is possible from such compositions to produce moulded elements, the shrinkage of which can practically be no longer measured. Even in most unfavourable cases, this shrinkage is only a few tenths of 1%.

The expression "plasticiser" as used herein refers to a group of substances which are known *per se*. However, the use of this expression is not intended to mean that the addition of these substances to the composition according to the invention is solely to produce a plasticising effect.

As already stated, the unsaturated polyester resins, which are used for the process according to the invention are those which can be strongly cross-linked, i.e. form many inter-molecular bonds when cured; they are compounds formed from a glycol or glycols and an acid or acids; either the alcohol or the acid, or both must be unsaturated. As the degree of cross-linking is higher, so is it possible to obtain better results as regards the reduction of the shrinkage. The strong cross-linking is for example recognisable from the thermal strength of the product or the many unsaturated bonds which exist concurrently with the strong cross-linking capacity and which can be directly determined analytically.

Thus the unsaturated polyester resins used in the present invention are those unsaturated polyester resins which have a proportion of double bonds corresponding to a bromine number of more than 6, preferably more than 8. It is preferred to use those normal commercial unsaturated polyester resins which have approximately the following data:

In the cured condition:—

Thermal stability under load 185 to 190° C.

Dimensional stability under heat (according to Vicat) > 150° C.

In the uncured condition:—

Refractive index $n_D = 1.500$.

Density at 20° C.: 1.1 g/ml.

Maximum hardening heat: about 120 cal/g.

Bromine number: 10.9.

It is however also possible successfully to use such unsaturated polyester resins which show approximately the following data:—

In the cured condition:—

Thermal stability under load from 80 to 182° C.

Dimensional stability under heat (according to Vicat) from 70 to 140° C.

In the uncured condition:—

Refractive index n_D from 1.500 to 1.560.

Density at 20° C.; from 1.10 to 1.20 g/ml.

Maximum hardening heat from about 75 to about 100 cal/g.

As plasticisers for the compositions according to the invention there are employed polyesters of polyhydric alcohols and polycarboxylic acids, generally speaking, it is however advantageous to use these plasticisers, in additions of 5 to 20% by weight, which is sufficient to produce the desired effect. This group includes for example the polyadipates i.e. esters of adipic acid and glycols, for example propylene glycol and adipic acid-butylene glycol polyesters, which are known *per se*. Polypropylene glycol adipic acid polyesters are preferably used.

If the unsaturated polyester resins referred to above have added thereto small quantities of these plasticisers, for example less than 3%, it is even possible for an increase in the shrinkage to occur, i.e. the measured shrinkage is higher than that which can be calculated on the basis of the ratio between non-shrinking plasticiser and the polyester hardened with contraction in the mixture. If the addition of plasticiser exceeds a predetermined value, a sudden steep fall takes place in the shrinkage values which often then can scarcely be measured. Since the occurrence of this sudden steep fall depends on the nature of the plasticiser and the nature of the unsaturated polyester resin, it is possible to adapt the decrease in shrinkage and the change in the mechanical properties to the particular purpose in question. Thus, it is for example possible so to adjust the shrinkage that it is able to compensate for the change in the dimensions of the casting mould being used, this change occurring because of the heat of reaction during the curing of the composition.

It is only possible in the process according to the invention to use those plasticisers which are completely miscible, i.e. produce a clear solution, with the unsaturated polyester resin and with the monomeric polymerisable compound. The plasticiser must also not separate out after a period of time. Apart from the effect which is connected herewith, this is also of importance in practice as regards the use of the compositions according to the invention, since otherwise the customer would be required to produce these mixtures only just before the compositions themselves are used. In addition, it is advantageous that these mixtures show no tendency to self-polymerisation. On the other hand, they must cause a clouding in the cured moulded elements, which can show all transitional stages from a light milky clouding to complete opaque white. The stronger this clouding,

5	Polyester pure	Monostyrene total	Plasticiser	Absolute longitudinal shrinkage				difference between measured and calculated shrinkage values	
				allowing for quantity of plasticiser					
				Pts. by weight	Pts. by weight	Pts. by weight	measured		calculated
				mm.	%	mm.	%	in %	percentage
10	53.5	45.8	—	3.25	13.0	—	—	—	—
	45.4	40.2	13.7	0.05	0.2	2.83	11.3	—11.1	—98
	44.5	39.8	15.0	0	0	2.78	11.1	—11.1	—100
	43.0	38.8	17.5	0	0	2.70	10.8	—10.8	—100
	41.5	37.8	20.0	0.05	0.2	2.63	10.5	—10.3	—98

EXAMPLE 2.

- 15 The procedure of Example 1 is followed, but using another adipic acid polyester (commercial product Ultramoll III (a Registered Trade Mark) of Farbenfabriken Bayer A.G.) as plasticiser. The polyester resin contains 40% of monomeric styrene and the total organic material is diluted with a further 10 parts by weight of monostyrene. 20.

25	Polyester resin in form as delivered	Plasticiser in	Absolute longitudinal shrinkage				Difference between measured and calculated shrinkage values	
			allowing for quantity of plasticiser					
			Pts. by weight	Pts. by weight	measured mm. ‰		calculated mm. ‰	
30	75.3	14	.095	3.8	2.80	11.2	—8.4	—75
	73.3	16	.055	2.2	2.76	11.0	—8.8	—80
	69.3	20	.065	2.6	2.63	10.5	—7.9	—75
	59.3	30	.030	1.2	2.31	9.2	—8.0	—87

EXAMPLE 3.

- 35 The procedure of Example 1 is followed, but using "Ultramoll II" of Farbenfabriken Bayer A.G. as plasticiser. The polyester resin contains 40% of monomeric styrene and total organic material is diluted with a further 40 parts by weight of monostyrene.

40	Absolute longitudinal shrinkage							
	Polyester resin in form in delivered	Plasticiser in	allowing for quantity of plasticiser				difference between measured and calculated shrinkage values	
45	Pts. by weight	Pts. by weight	measured mm.	%	calculated mm.	%	absolute in %	percentage
	76.2	13.1	1.45	5.8	2.84	11.3	—5.5	—49
	75.6	13.7	1.40	5.6	2.83	11.3	—5.7	—50
	74.3	15.0	0	0	2.78	11.1	—11.1	—100

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EXAMPLE 4.

- 55 The procedure of Example 1 is followed, but using adipic acid-butylene glycol polyester (commercial product Weichmacher ABG of Bad. Anilin- u. Soda-Fabr.) is used as plasticiser. The polyester resin contains 40% of monomeric styrene and the total organic material is diluted with a further 10 parts by weight of monostyrene.

the smaller, general, is the shrinkage which occurs. Clear polymers are homogeneous and show shrinkage if the clarity is not to be attributed to like refractive indices. This phenomenon provides the person skilled in the art with a simple means for finding the correct mixture. It is obvious that such preliminary experiments must be conducted without use of fillers.

It is for example possible to employ vinyl toluene, or, preferably, styrene, as monomeric polymerisable compounds containing a vinyl group. Generally speaking, these compounds are used in quantities which are from 30 to 50% by weight, calculated on the total weight of organic material. These are quantities which may be present in normal commercial polyester mixtures. In many cases, it is however advantageous to increase or reduce these quantities, for example by 20% by weight. As is known, all monomeric compounds of this type show a considerable shrinkage during polymerisation. It was therefore to be expected that the increase in this proportion would also increase the total shrinkage of the mixture. It was quite surprising that actually the opposite is the case. The sudden steep decrease in the shrinkage can be displaced in both directions by altering the quantity of monomeric compound containing a vinyl group, depending on the plasticiser being used. This provides an additional possibility of varying the properties of the moulded elements.

The compositions according to the invention will preferably have added thereto fillers in quantities up to 85% by weight, advantageously up to 80% by weight, based on the total composition. It is possible to use all known fillers of any desired particle size, such as powdered quartz, powdered stone, glass powder and barium sulphate, as well as finely divided metal or metalloid oxides which have been obtained by the oxidation or hydrolytic decomposition of volatile metal or metalloid compounds in the gas phase at elevated temperature.

Redox systems which consist of a peroxidic compound and a secondary or tertiary amine and/or an amine salt and/or an α -amino sulphone and/or α -hydroxy sulphones, are used as catalyst. Benzoyl peroxide and 4,4'-dichlorodibenzoyl peroxide can more especially be used as peroxide compounds.

It is generally preferred to use those tertiary amines which contain at least one aromatic radical, and diisopropylol-*p*-toluidine or dimethyl-*p*-toluidine and dimethyl aniline are particularly suitable for use. Polymerisation accelerators which are known *per se*, such as heavy metal compounds with a labile halogen atom, can be added. Such compositions can be hardened in an extremely short time without using heat or pressure.

The invention is further illustrated by the following Examples: (all parts and percentages are by weight).

EXAMPLE 1.

A filling, casting and moulding composition which has the composition shown in the Table and in addition contains 0.2 parts by weight of diisopropylol-*p*-toluidine, 0.033 part by weight of hydroquinone and 0.5 part by weight of paraffin wax, is mixed with 72% barium sulphate. For curing purposes, 1 part by weight of a hardener paste consisting of equal quantities of benzoyl peroxide and plasticiser is added. The composition is poured into a casting mould with the dimensions 250 × 50 × 20 mm. The processing time is 25 to 30 minutes. The moulded element can be removed after 1½ hours: it is seen to be opaque. The longitudinal shrinkage measured after 1 day is indicated in the following Table. A polypropylene glycol adipic acid polyester (commercial product Hexaplas PPA (a Registered Trade Mark) of I.C.I.) was used as plasticiser. The polyester (commercial product Palatal P 7 of B.A.S.F.) showed the following data:

Composition: A 30% solution in styrene of a compound derived from equimolar amounts of maleic acid and propan-1,2-diol.

In the cured condition:—

Thermal stability under load 185 to 190° C.

Dimensional stability under heat (according to Vicat) 150° C.

In the uncured condition:—

Refractive index $n_D = 1.5$.

Density at 20° C.: 1.100 g/ml.

Maximum hardening heat: about 120 cal./g.

Bromine number: 10.9.

Polyester resin in form of delivered	Plasticiser in	Absolute longitudinal shrinkage		allowing for quantity of plasticiser		difference between measured and calculated shrinkage values	
		Pts. by weight	Pts. by weight	measured mm.	calculated mm.	absolute in ‰	percentage
5	10	79.3	10	0.05	0.2	2.95	11.8
	15	74.3	15	0	0	2.78	11.1
	20	69.3	20	0.1	0.4	2.63	10.5
						—11.6	—98
						—11.1	—100
						—10.1	—96

EXAMPLE 5.

- The procedure of Example 1 is followed, but using different polyester resins which are mixed with about 35 to 40% by weight of styrene. 25 parts by weight of another adipic acid polyester (commercial product Hexaplas PPA of I.C.I.) are used as plasticiser. The compositions contain 65% barium sulphate, except that 72% were used in Experiment No. 2. The polyester resins show the following data:—
- (1) Refractive index: 1.56.
Dimensional stability under heat according to Vicat: 130° C.
Density at 20° C.: 1.14 g./cm³.
(Commercial product Leguval T20 [a Registered Trade Mark] of Farbenfabriken Bayer A.G.).
- (2) Refractive index $n_D = 1.534$.
Density at 20° C.: 1—128 g./ml.
Maximum hardening heat: about 100 cal./g.
Mean thermal stability under load: 125° C.
Dimensional stability under heat according to Vicat: 140° C.
Bromine number: 7.8.
(Commercial product Palatal P6 [a Registered Trade Mark] of B.A.S.F.).
- It contained 30% of styrene and 70% of a polyester derived from maleic acid, *o*-phthalic acid and propan-1, 2-diol in the proportions 1:1:2.
- (3) Refractive index $n_D = 1.545$.
Density at 20° C.: 1.120.
Maximum hardening heat: about 75 cal./g.
Mean thermal stability under load: 83° C.
Dimensional stability under heat according to Vicat: 80° C.
(Commercial product Palatal P4 of B.A.S.F.).
- (4) Refractive index: 1.56.
Thermal stability under load according to Vicat: 182° C.
Density at 20° C.: 1.12 g./ml.
(Commercial product Leguval K25/R of Farbenfabriken Bayer A.G.).
- (5) Refractive index: 1.550.
Density at 20° C.: 1.150 g./ml.
Mean thermal stability under load: 80° C.
Dimensional stability under heat according to Vicat: 70° C.
(Commercial product Palatal P5 of B.A.S.F.).
- (6) Density at 20° C.: 1.112.
Thermal stability according to Marten: about 120° C.
Refractive index (hardened): 1.541.
(Commercial product Roskydal WSF [a Registered Trade Mark] of Farbenfabriken Bayer A.G.).

75	Absolute longitudinal shrinkage						
	Polyester in form as delivered	allowing for quantity of plasticiser				Difference between measured and calculated shrinkage values	
80	Pts. by weight	measured mm.	%	calculated mm.	%	absolute in %	percentage
	(1) 74.2	0.06	2.4	1.12	4.5	—2.0	—45
	(2) 74.3	1.05	4.2	1.63	6.5	—2.2	—34
	(3) 74.3	0.85	3.4	1.75	7.0	—3.6	—52
	(4) 74.5	1.0	4.0	2.13	8.5	—4.5	—53
85	(5) 74.3	0.60	2.4	1.86	7.4	—5.0	—68
	(6) 74.2	0.70	2.8	2.09	8.4	—5.6	—67

EXAMPLE 6.

The procedure of Experiment 6, Example 5, is followed, but using 20% by weight of plasticiser. The measured longitudinal shrinkage is lowered by 82% of the calculated value.

EXAMPLE 7.

The procedure of Experiment 5, Example 5, is followed, but in addition 10 parts by weight of styrene are added to the organic material. The measured longitudinal shrinkage is lowered by 89% of the calculated value.

WHAT WE CLAIM IS:—

1. A filling, casting and moulding composition which can be cured, without shrinking, by free-radical catalysts known *per se*, which comprises (a) from 10 to 70% by weight, based on the total weight of organic material, of at least one monomeric, polymerisable organic compound containing a vinyl group, (b) at least one unsaturated, curable polyester resin, which has a proportion of double bonds corresponding to a bromine number greater than 6, (c) from 3 to 30% by weight, based on the total weight of organic material, of a saturated polyester plasticiser, miscible with the organic components of the composition before curing but not completely miscible with the cured mixture, and (d) a redox catalyst system containing one or more reducing agents.

2. A composition as claimed in Claim 1 which contains also fillers.

3. A composition as claimed in Claims 1 or 2 which comprises also a polymerisation accelerator.

4. A composition as claimed in Claim 3 wherein the accelerator comprises a heavy metal compound and/or a compound with a labile chlorine atom.

5. A composition as claimed in any of Claims 1 to 4 in which the plasticiser comprises 3 to 20% of the total weight of organic material.

6. A composition as claimed in any of Claims 1 to 5 in which the plasticiser is a polyester of propylene glycol and adipic acid.

7. A composition as claimed in any of Claims 1 to 6 in which contains up to 85% by weight of fillers.

8. A composition as claimed in any of Claims 1 to 7 in which the redox catalyst consists of a peroxidic compound and a secondary or tertiary amine and/or amine salt and/or α -aminosulphone and/or α -hydroxysulphone.

9. A composition as claimed in Claim 8 in which the redox system comprises a tertiary amine with at least one aromatic radical.

10. A composition as claimed in Claim 1 substantially as described with reference to any of the Examples.

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